federal register

Wednesday
October 15, 1980

Part III

Environmental Protection Agency

National Emission Standards for Hazardous Air Pollutants; Test Methods

ENVIRONMENTAL PROTECTION AGENCY

40 CFR Part 61

[AR-FRL 1553-6]

National Emission Standards for Hazardous Air Pollutants; Test Methods; Revisions and Addition

AGENCY: Environmental Protection Agency (EPA).

ACTION: Proposed rule and notice of public hearing.

SUMMARY: The purpose of this action is to propose revisions to Methods 101 and 102 for chlor-alkali plants and to propose Method 111 for sewage sludge incinerators. On April 6, 1973 (38 FR 8820), the Environmental Protection Agency promulgated national emission standards for hazardous air pollutants asbestos, beryllium, and mercury. An appendix to the regulation contained Methods 101 and 102, which prescribed testing and analytical procedures for mercury emissions. Since their promulgation, the test methods have been evaluated by EPA at chlor-alkali plants and sewage sludge incinerators. Several modifications and clarifications to the procedures were found to be necessary to improve the precision and accuracy of the method. Some of these changes, coupled with the low mercury levels in the effluent of the sewage sludge incinerators, indicated the need for a new method for this source. Methods 101 and 102 are also revised to make them consistent with the latest revisions to Method 5 (42 FR 41754) of 40 CFR Part 60—Appendix A, since many parts of the methods are similar.

DATES: *Comments.* Comments must be received (in duplicate if possible) on or before December 15, 1980.

Public Hearing. A public hearing will be held on November 6, 1980 (about 30 days after proposal) beginning at 9:00 a.m.

Request to Speak at Hearings. Persons wishing to present oral testimony must contact EPA by October 30, 1980 (1 week before hearing).

ADDRESSES: *Comments.* Comments should be submitted (in duplicate if possible) to the Central Docket Section (A-130), Attention: Docket Number A-79-45, U.S. Environmental Protetion Agency, 401 M Street, S.W., Washington, D.C. 20460.

Public Hearing. The public hearing will be held at Emission Measurement Lab, RTP, NC. Persons wishing to present oral testimony should notify Ms. Deanna Tilley, Standards Development Branch (MD-13), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, telephone number (919) 541-5421.

Docket. Docket Number A-79-45, containing material relevant to this rulemaking, is located in the U.S. Environmental Protection Agency, Central Docket Section, West Tower Lobby, Gallery 1, Waterside Mall, 401 M Street, S.W., Washington, D.C. 20460. The docket may be inspected between 8 a.m. and 4 p.m. on weekdays, and a reasonable fee may be charged for copying.

FOR FURTHER INFORMATION CONTACT: Mr. Roger Shigehara (MD-19), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, telephone number (919) 541-2237.

SUPPLEMENTARY INFORMATION: Changes common to Methods 101 and 102 are formatted to make the methods consistent with Method 5 of 40 CFR Part 60. These methods are quite similar, and Method 5 is now widely used. Having Methods 101 and 102 make reference to Method 5 and to each other shortens the methods considerably. Specific changes to Method 101 are as follows:

1. An aliquot of the collected sample is diluted with 5 percent sulfuric acid solution instead of 0.1 M iodine monochloride. This step removes the cause of nonreproducible blanks and calibration shifts and also removes the need to neutralize the sample with 10 N sodium hydroxide before analysis.

2. Construction details of the aeration and optical cells are provided in the method. This design prevents the loss of mercury between the time that the reducting agent is added and the aeration bottle is attached to the aeration system.

3. Further details are given to prevent condensation of water and mercury in the aeration system.

4. When a filter is used ahead of the impingers, a wire-screen filter support is used instead of a glass frit support to avoid the loss of mercury in the frit.

Method 111 for sewage sludge incinerators is required because, for accurate analysis, the iodine monochloride concentration in the aeration system cannot exceed 0.0001 M, as higher concentrations inhibit the reduction of mercury. This restriction, coupled with the low mercury levels present in the samples taken from the effluent of sewage sludge incinerators, caused the revised Method 101 to be unsuitable for most sewage sludge incinerator stack samples. Thus, a new method that uses potassium permanganate as the collecting liquid is being proposed.

(Secs. 112, 114, and 301(*a) of the Clean Air Act as amended (42 U.S.C. 7412, 7414, and 7601(a))

Dated: October 6, 1980.

Douglas M. Costle,

Administrator.

It is proposed that 40 CFR Part 61, Appendix B—Test Methods, be amended by revising Methods 101 and 102 and by adding Method 111 as follows:

1. By revising Methods 101 and 102 of Appendix B—Test Methods as follows:

Appendix B—Test Methods

Method 101. Determination of Particulate and Gaseous Mercury Emissions from Chlor-Alkali Plants—Air Streams

1. *Applicability and Principle.*

1.1 Applicability. This method applies to the determination of particulate and gaseous mercury (Hg) emissions from chlor-alkali plants and other sources (as specified in the regulations), where the carrier-gas stream in the duct or stack is principally air.

1.2 Principle. Particulate and gaseous Hg emissions are withdrawn isokinetically from the source and collected in acidic iodine monochloride (ICl) solution. The Hg collected (in the mercuric form) is reduced to elemental Hg, which is then aerated from the solution into an optical cell and measured by atomic absorption spectrophotometry.

2. *Range and sensitivity.*

2.1 Range. After initial dilution, the range of this method is 0.5 to 120 μg Hg/ml. The upper limit can be extended by further dilution of the sample.

2.2 Sensitivity. The sensitivity of this method depends on the recorder/spectrophotometer combination selected.

3. *Interfering Agents.*

3.1 Sampling. SO_2 reduces ICl and causes premature depletion of the ICl solution.

3.2 Analysis. ICl concentrations greater than 10^{-4} molar inhibit the reduction of the Hg(II) ion in the aeration cell. Condensation of water vapor on the optical cell windows causes a positive interference.

4. *Precision and Accuracy.*

The following estimates are based on collaborative tests, wherein 13 laboratories performed duplicate analyses on two Hg-containing samples from a chlor-alkali plant and on one laboratory-prepared sample of known Hg concentration. The concentrations ranged from 2 to 65 μg Hg/ml.

4.1 Precision. The estimated within-laboratory and between-laboratory

standard deviations are 1.6 and 1.8 μg Hg/ml, respectively.

4.2 Accuracy. The participating laboratories that analyzed a 64.3-μg Hg/ml (in 0.1 M ICl) standard obtained a mean of 63.7 μg Hg/ml.

5. *Apparatus.*

5.1 Sampling Train. A schematic of the sampling train is shown in Figure 101–1; it is similar to the Method 5 train. The sampling train consists of the following components:

5.1.1 Probe Nozzle, Pitot Tube, Differential Pressure Gauge, Metering System, Barometer, and Gas Density Determination Equipment. Same as Method 5, Sections 2.1.1, 2.1.3, 2.1.4, 2.1.8, 2.1.9, and 2.1.10, respectively.

5.1.2 Probe Liner. Borosilicate or quartz glass tubing. The tester may use a heating system capable of maintaining a gas temperature of 12 ± 14°C (248 ± 25°F) at the probe exit during sampling to prevent water condensation.

Note.—Do not use metal probe liners.

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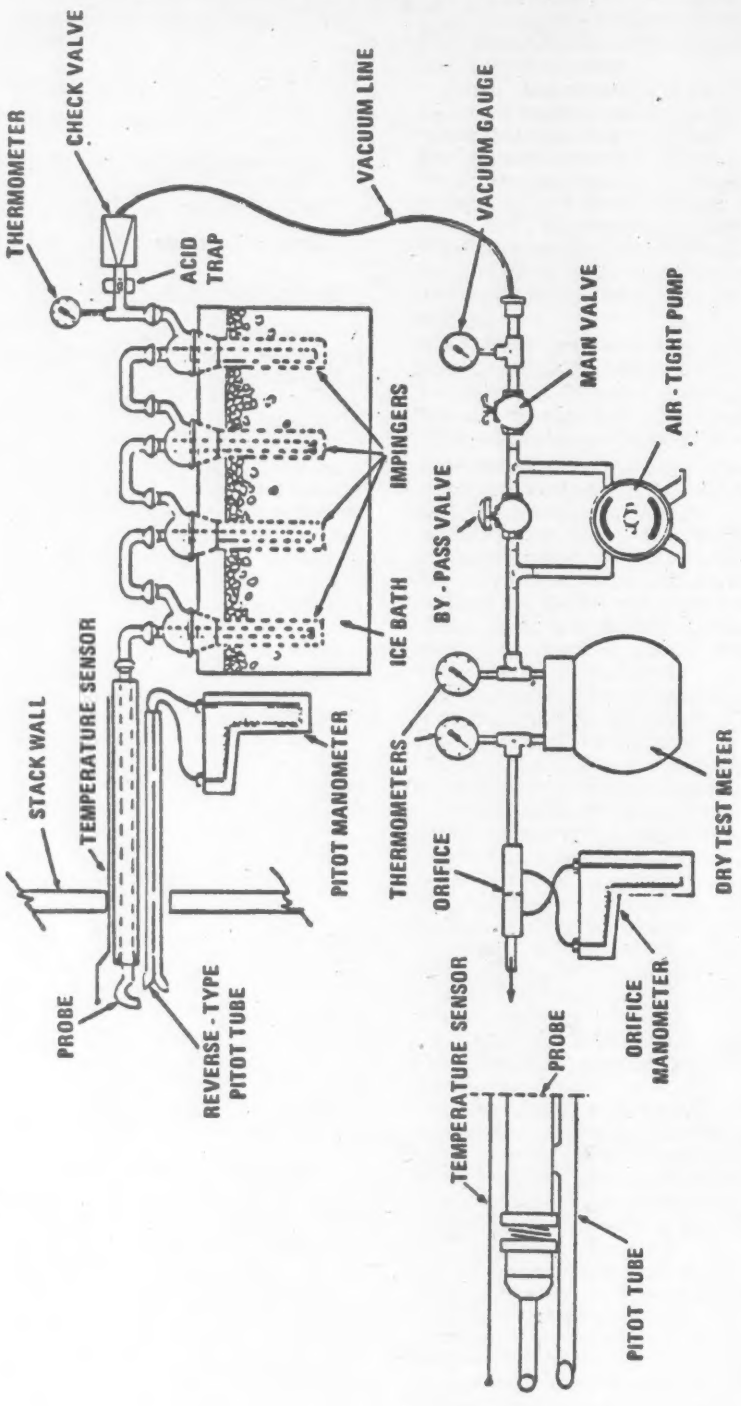

Figure 101-1 Mercury sampling train.

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5.1.3 Impingers. Four Greenburg-Smith impingers connected in series with leak-free ground glass fittings or any similar lead-free noncontaminating fittings. For the first, third, and fourth impingers, the tester may use impingers that are modified by replacing the tip with a 13-mm-ID (0.5-in.) glass tube extending to 13 mm (0.5 in.) from the bottom of the flask.

5.1.4 Acid Trap. Mine Safety Appliances [1] Air Line Filter, Catalogue Number 81857, with acid absorbing cartridge and suitable connections, or equivalent.

5.2 Sample Recovery. The following items are needed:

5.2.1 Glass Sample Bottles. Leakless, with Teflon-lined caps, 1000- and 100-ml.

5.2.2 Graduated Cylinder. 250-ml.

5.2.3 Funnel and Rubber Policeman. To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

5.2.4 Funnel. Glass, to aid in sample recovery.

5.3 Sample Preparation and Analysis. The following equipment is needed:

5.3.1 Atomic Absorption Spectrophotometer. Perkin-Elmer 303, or equivalent, containing a hollow-cathode mercury lamp and the optical cell described in section 5.3.2.

5.3.2 Optical Cell. Cylindrical shape with quartz end windows and having the dimensions shown in Figure 101–2. Wind the cell with approximately 2 meters of 24-guage nichrome heating wire, and wrap with asbestos insulation tape or equivalent; do not let the wires touch each other.

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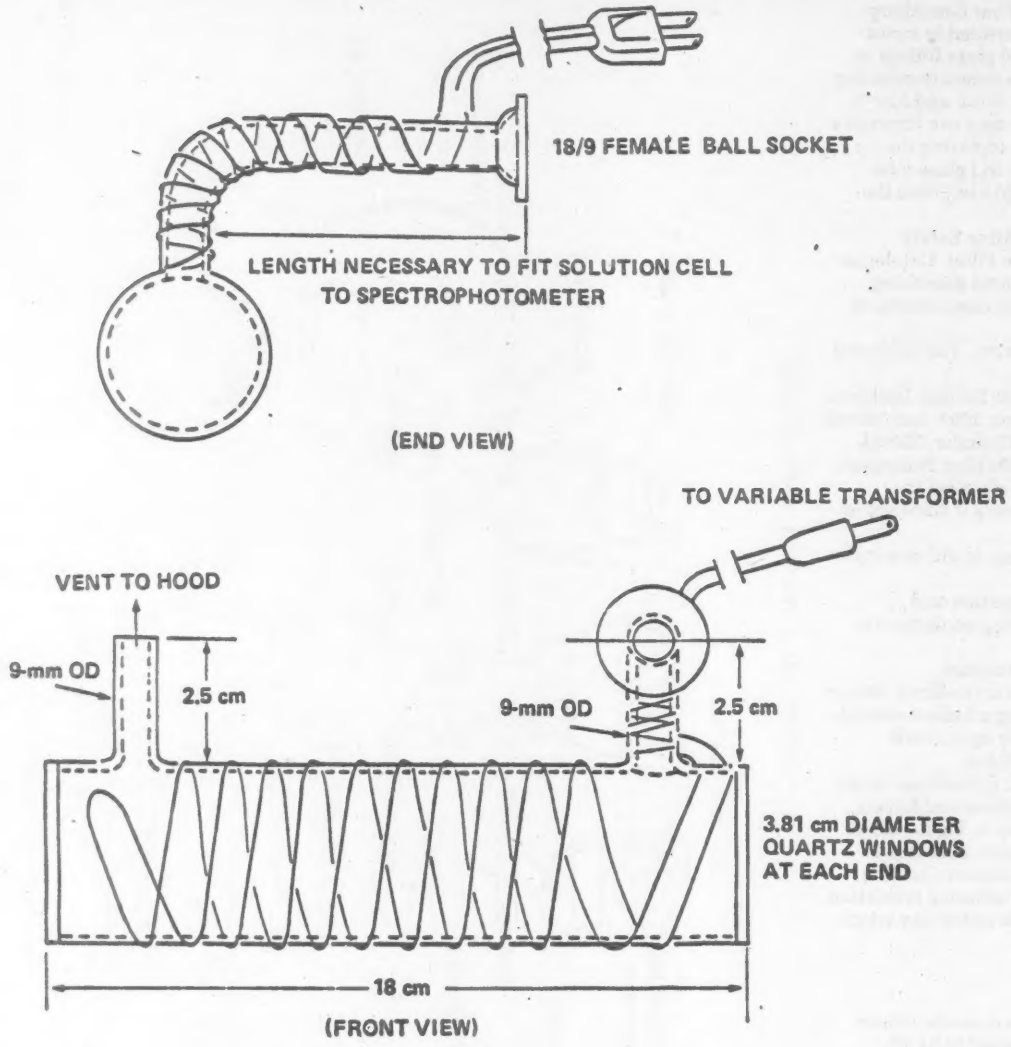
[1] Mention of trade names or specific products does not constitute endorsement by the U.S. Environmental Protection Agency



NOTES:
CELL WOUND WITH 24-GAUGE NICHROME WIRE
TOLERANCES ± 5 PERCENT

Figure 101-2. Optical cell.

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5.3.3 Aeration Cell. Constructed according to the specifications in Figure 101–3. Do not use a glass frit as a substitute for the blown glass bubbler tip shown in Figure 101–3.

5.3.4 Recorder. Matched to output of the spectrophotometer described in section 5.3.1.

5.3.5 Variable Transformer. To vary the voltage on the optical cell from 0 to 40 volts.

5.3.6 Hood. For venting optical cell exhaust.

5.3.7 Flow Metering Valve.

5.3.8 Flow Meter, Rotameter or equivalent, capable of measuring a gas flow of 1.5 liters/min.

5.3.9 Nitrogen/Cylinder. Equipped with a single-stage regulator.

5.3.10 Connecting Tubing. Use glass tubing (ungreased ball- and socket-connections are recommended) for all tubing connections between the solution cell and the optical cell; do not use Tygon tubing, other types of flexible tubing, or metal tubing as substitutes. The tester may use Teflon, steel, or copper tubing between the nitrogen tank and flow metering valve (5.3.7), and Tygon, gum, or rubber tubing between the flow metering valve and the aeration cell.

5.3.11 Flow Rate Calibration Equipment. Bubble flow meter or wet test meter for measuring a gas flow rate of 1.5 ± liters/min.

5.3.12 Volumetric Flasks. Class A with penny head standard taper stoppers; 100-, 250-, 500-, and 1000-ml.

5.3.13 Volumetric Pipets. Class A; 1-, 2-, 3-, 4-, and 5-ml.

5.3.14 Graduated Cylinder. 50-ml.

5.3.15 Magnetic Stirrer. General-purpose laboratory type.

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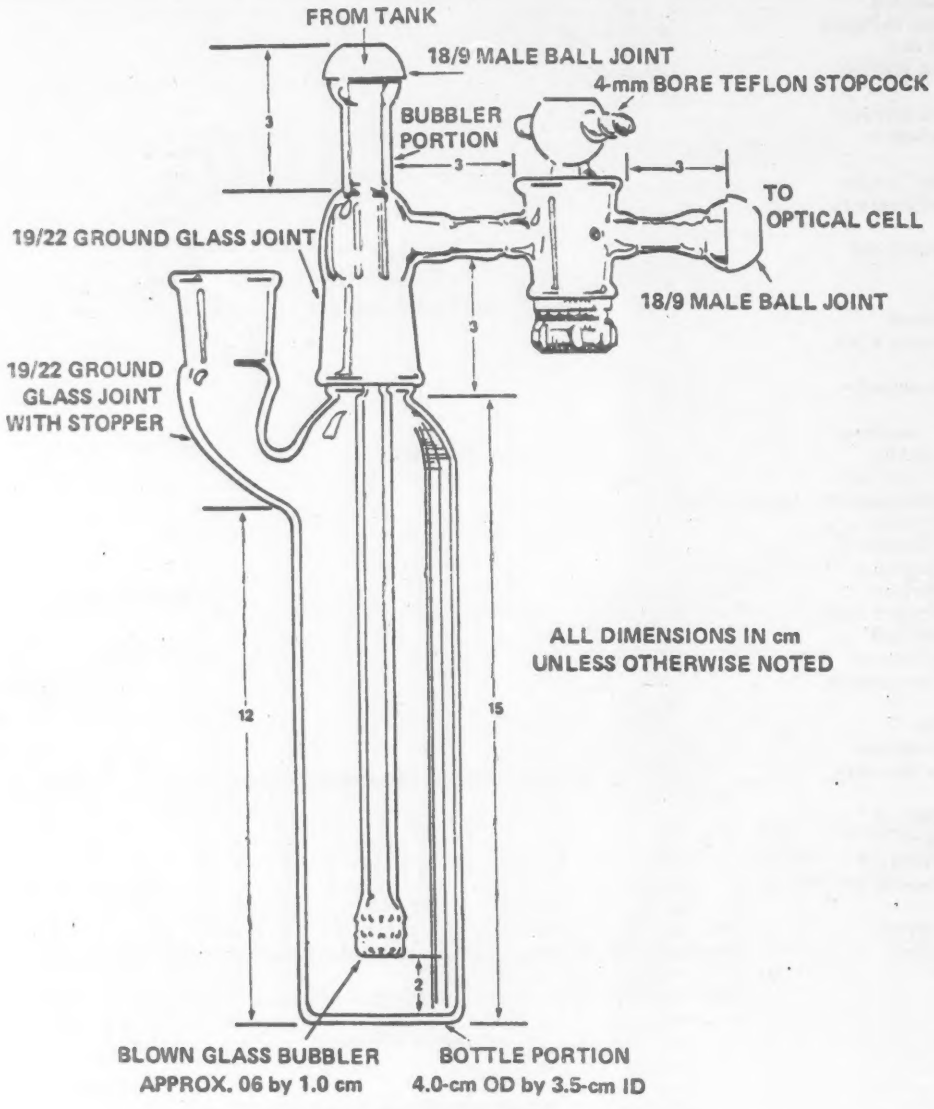

Figure 101-3. Aeration cell.

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5.3.16 Magnetic Stirring Bar. Teflon-coated.

5.3.17 Balance. Capable of weighing to ±0.5 g.

6. *Reagents.*

Use ACS reagent-grade chemicals or equivalent, unless otherwise specified.

6.1 Sampling and Recovery. The reagents used in sampling and recovery are as follows:

6.1.1 Water. Deionized distilled, meeting STM Specifications for Type I Reagent Water-ASTM Test Method D 1193–72. If high concentrations of organic matter are not expected to be present, the analyst may eliminate the $KMnO_4$ test for oxidizable organic matter. Use this water in all dilutions and solution preparations.

6.1.2 Nitric Acid (HNO_3), 50 Percent (V/V). Mix equal volumes of concentrated HNO_3 and deionized distilled water.

6.1.3 Silica Gel. Indicating type, 6– to 16–mesh. If previously used, dry at 175°C (350°F) for 2 hrs. The tester may use new silica gel as received.

6.1.4 Potassium Iodide (KI) Solution, 25 Percent. Dissolve 250 g of KI in deionized distilled water and dilute to 1 liter.

6.1.5 Iodine Monochloride (ICl) Stock Solution, 1.0 M. to 800 ml of 25 percent KI solution, add 800 ml of concentrated hydrochloric acid (HCl). Cool to room temperature. With vigorous stirring, slowly add 135 g of potassium iodate (KIO_3) and stir until all free iodine has dissolved. A clear orange-red solution occurs when all the KIO_3 has been added. Cool to room temperature and dilute to 1800 ml with deionized distilled water. Keep the solution in amber glass bottles to prevent degradation.

6.1.6 Absorbing Solution, 0.1 M ICl. Dilute 100 ml of the 1.0 M ICl stock solution to 1 liter with deionized distilled water. Keep the solution in amber glass bottles and in darkness to prevent degradation. This reagent is stable for at least 2 months.

6.2 Sample Preparation and Analysis. The reagents needed are listed below:

6.2.1 Tin(II) Solution. Prepare fresh daily and keep sealed when not being used. Completely dissolve 20 g of tin(II) chloride (or 25 g of tin(II) sulfate) crystals (Baker Analyzed reagent grade or any other brand that will give a clear solution) in 25 ml of concentrated HCl. Dilute to 250 ml with deionized distilled water. Do not substitute HNO_3, H_2SO_4, or other strong acids for the HCl.

6.2.2 Mercury Stock Solution, 1 mg Hg/ml. Completely dissolve 0.1354 g of mercury (II) chloride in 75 ml of deionized distilled water. Add 10 ml of concentrated HNO_3, and adjust the volume to exactly 100 ml with deionized distilled water. Mix thoroughly. This solution is stable for at least 1 month.

6.2.3 Sulfuric Acid, 5 Percent (V/V). Dilute 25 ml of concentrated H_2SO_4 to 500 ml with deionized distilled water.

6.2.4 Intermediate Mercury Standard Solution, 10 μg Hg/ml. Prepare fresh weekly. Pipet 5.0 ml of the mercury stock solution (6.2.2) into a 500–ml volumetric flask and add 20 ml of the 5 percent H_2SO_4 solution. Dilute to exactly 500 ml with deionized distilled water. Thoroughly mix the solution.

6.2.5 Working Mercury Standard Solution, 200 ng Hg/ml. Prepare fresh daily. Pipet 5.0 ml from the "Intermediate Mercury Standard Solution" (6.2.4) into a 250-ml volumetric flask. Add 10 ml of the 5 percent H_2SO_4 and 2 ml of the 0.1 M ICl absorbing solution taken as a blank (7.2.5) and dilute to 250 ml with deionized distilled water. Mix thoroughly.

7. *Procedure.*

7.1 Sampling. Because of the complexity of this method, testers should be trained and experienced with the test procedures to assure reliable results. Since the amount of Hg that is collected generally is small, the method must be carefully applied to prevent contamination or loss of sample.

7.1.1 Pretest Preparation. Follow the general procedure given in Method 5, section 4.1.1, except omit the directions on the filter.

7.1.2 Preliminary Determinations. Follow the general procedure given in Method 5, section 4.1.2, except as follows: Select a nozzle size based on the range of velocity heads to assure that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates below 28 liters/min (1.0 cfm).

Obtain samples over a period or periods that accurately determine the maximum emissions that occur in a 24-hr period. In the case of cyclic operations, run sufficient tests for the accurate determination of the emissions that occur over the duration of the cycle. A minimum sample time of 2 hrs. is recommended. In some instances, high Hg or high SO_2 concentrations make it impossible to sample for the desired minimum time. This is indicated by reddening (liberation of free iodine) in the first impinger. In these cases, the tester may divide the sample run into two or more subruns to insure that the absorbing solution is not depleted.

7.1.3 Preparation of Sampling Train. Clean all glassware [probe, impingers, and connectors] by rinsing with 50 percent HNO_3, tap water, 0.1 M ICl, tap water, and finally deionized distilled water. Place 100 ml of 0.1 M ICl in each of the first three impingers. Take care to prevent the absorbing solution from contacting any greased surfaces. Place approximately 200 g of preweighed silica gel in the fourth impinger. The tester may use more silica gel, but should be careful to ensure that it is not entrained and carried out from the impinger during sampling. Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, determine and record the weight of the silica gel plus impinger to the nearest 0.5 g.

Install the selected nozzle using a Viton A O–ring when stack temperatures are less than 260°C (500°F). Use an asbestos string gasket if temperatures are higher. See APT–0576 [2] for details. Other connecting systems using either 316 stainless steel or Teflon ferrules may be used. Mark the probe with heat-resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point. Assemble the train as shown in Figure 101–1, using (if necessary) a very light coat of silicone grease on all ground glass joints. Grease only the outer portion (see APTD–0576) to avoid possibility of contamination by the silicone grease.

Note.—An empty impinger may be inserted between the third impinger and the silica gel to remove excess moisture from the sample stream.

After the sampling train has been assembled, turn on and set the probe, if applicable, at the desired operating temperature. Allow time for the temperatures to stabilize. Place crushed ice around the impingers.

7.1.4 Leak-Check Procedures. Follow the leak-check procedures outlined in Method 5, sections 4.1.4.1 (Pretest Leak Check), 4.1.4.2 (Leak Checks During Sample Run), and 4.1.4.3 (Post-Test Leak Check).

7.1.5 Mercury Train Operation. Follow the general procedure given in Method 5, section 4.1.5. For each run, record the data required on a data sheet such as the one shown in Figure 101–4.

7.1.6 Calculation of Percent Isokinetic. Same as Method 5, section 4.1.6.

7.2 Sample Recovery. Begin proper cleanup procedure as soon as the probe is removed from the stack at the end of the sampling period.

Allow the probe to cool. When it can be safely handled, wipe off any external

[2] Rom, Jerome, J. Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment. U.S. Environmental Protection Agency. Research Triangle Park, NC. Publication No. APTD–0576. March 1972.

particulate matter near the tip of the probe nozzle and place a cap over it. Do not cap off the probe tip tightly while the sampling train is cooling. Capping would create a vacuum and draw liquid out from the impingers.

Before moving the sampling train to the cleanup site, remove the probe from the train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the impinger. Use either ground-glass stoppers, plastic caps, or serum caps to close these openings.

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PLANT _____
LOCATION _____
OPERATOR _____
DATE _____
RUN NO. _____
SAMPLE BOX NO. _____
FILTER BOX NO. _____
METER ΔH@ _____
C FACTOR _____
PITOT TUBE COEFFICIENT, C_p _____

SCHEMATIC OF STACK CROSS SECTION

AMBIENT TEMPERATURE _____
BAROMETRIC PRESSURE _____
ASSUMED MOISTURE, % _____
PROBE LENGTH, m (ft) _____
NOZZLE IDENTIFICATION NO. _____
AVERAGE CALIBRATED NOZZLE DIAMETER, cm (in.) _____
PROBE HEATER SETTING* _____
LEAK RATE, m^3/min (cfm) _____
PROBE LINER MATERIAL _____
STATIC PRESSURE, mm Hg (in. Hg) _____
FILTER NO.* _____

TRAVERSE POINT NUMBER	SAMPLING TIME (θ), min.	VACUUM mm Hg (in. Hg)	STACK TEMPERATURE (T_S) °C (°F)	VELOCITY HEAD (ΔP_S)	PRESSURE DIFFERENTIAL ACROSS ORIFICE METER mm H_2O (in. H_2O)	GAS SAMPLE VOLUME m^3 (ft^3)	GAS SAMPLE TEMPERATURE AT DRY GAS METER		FILTER HOLDER* TEMPERATURE, °C (°F)	TEMPERATURE OF GAS LEAVING CONDENSER OR LAST IMPINGER, °C (°F)
							INLET °C (°F)	OUTLET °C (°F)		
TOTAL							Avg.	Avg.		
AVERAGE							Avg.			

*IF APPLICABLE

Fig. 101-4. Mercury field data.

BILLING CODE 6560-01-C

Transfer the probe and impinger assembly to a cleanup area that is clean, protected from the wind, and free of Hg contamination. The ambient air in laboratories located in the immediate vicinity of Hg-using facilities is not normally free of Hg contamination.

Inspect the train before and during assembly, and note any abnormal conditions. Treat the sample as follows:

7.2.1 *Container No. 1* (Impinger and Probe). Using a graduated cylinder, measure the liquid in the first three impingers to within ±1 ml. Record the volume of liquid present (e.g., see Figure 5–3 of Method 5). This information is needed to calculate the moisture content of the effluent gas. (Use only glass storage bottles and graduated cylinders that have been precleaned as in section 7.1.3.) Place the contents of the first three impingers into a 1000-ml glass sample bottle.

Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover the Hg (and any condensate) from the probe nozzle, probe fitting, and probe liner as follows: Rinse these components with two 50-ml portions of 0.1 M ICl. Next, rinse the probe nozzle, fitting and liner, and each piece of connecting glassware between the probe liner and the back half of the third impinger with a maximum of 400 ml of deionized distilled water. Add all washings to the 1000-ml glass sample bottle containing the liquid from the first three impingers.

After all washings have been collected in the sample container, tighten the lid on the container to prevent leakage during shipment to the laboratory. Mark the height of the liquid to determine later whether leakage occurred during transport. Label the container to clearly identify its contents.

7.2.2 *Container No. 2* (Silica Gel). Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. Transfer the silica gel from its impinger to its original container and seal. The tester may use as aids a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. The small amount of particles that may adhere to the impinger wall need not be removed. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g; record this weight.

7.2.3 *Container No. 3* (Absorbing Solution Blank). For a blank, place 50 ml of the 0.1 M ICl absorbing solution in a 100-ml sample bottle. Seal the container. Use this blank to prepare the working mercury standard solution (6.2.5).

7.3 Sample Preparation. Check the liquid level in each container to see whether liquid was lost during transport. If a noticeable amount of leakage occurred, either void the sample or use methods subject to the approval of the Administrator to account for the losses. Then follow the procedures below:

7.3.1 *Container No. 1* (Impinger and Probe). Carefully transfer the contents of Container No. 1 into a 1000-ml volumetric flask and adjust the volume to exactly 1000 ml with deionized distilled water.

7.3.2 Dilutions. Pipet 2 ml of the solution from 7.3.1 into separate 250-ml volumetric flasks. Add 10 ml of 5 percent H_2SO_4 to each flask and adjust the volumes to exactly 250 ml with deionized distilled water. These solutions are stable for at least 72 hr.

Note.—The dilution factor will be 250/2 for this solution.

7.4 Analysis. Calibrate the spectrophotometer and recorder and prepare the calibration curve as described in sections 8.1 to 8.4.

7.4.1 Mercury Samples. Repeat the procedure used to establish the calibration curve with appropriately sized aliquots (1 to 5 ml) of each of the diluted samples (from section 7.3.2) until two consecutive peak heights agree within ±3 percent of their average value. The peak maximum of an aliquot (except the 5-ml aliquot) must be greater than 10 percent of the recorder full scale. If the peak maximum of a 1.0-ml aliquot is off scale on the recorder, further dilute the original source sample to bring the Hg concentration in the calibration range of the spectrophotometer.

Run a blank and standard at least after every five samples to check the spectrophotometer calibration; recalibrate as necessary.

It is also recommended that at least one sample from each stack test be checked by the Method of Standard Additions to confirm that matrix effects have not interfered in the analysis.

7.4.2 *Container No. 2* (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. (This step may be conducted in the field.)

8. *Calibration and Standards.*

Before use, clean all glassware, both new and used, as follows: brush with soap and water, liberally rinse with tap water, soak for 1 hour in 50 percent HNO_3, and then rinse with deionized distilled water.

8.1 Flow Calibration. Assemble the aeration system as shown in Figure 101–5. Set the outlet pressure on the nitrogen cylinder regulator to a minimum pressure of 500 mm Hg (10 psi), and use the flow metering valve and a bubble flow meter or wet test meter to obtain a flow rate of 1.5 ± 0.1 liters/min through the aeration cell. After the flow calibration is complete, remove the bubble flow meter from the system.

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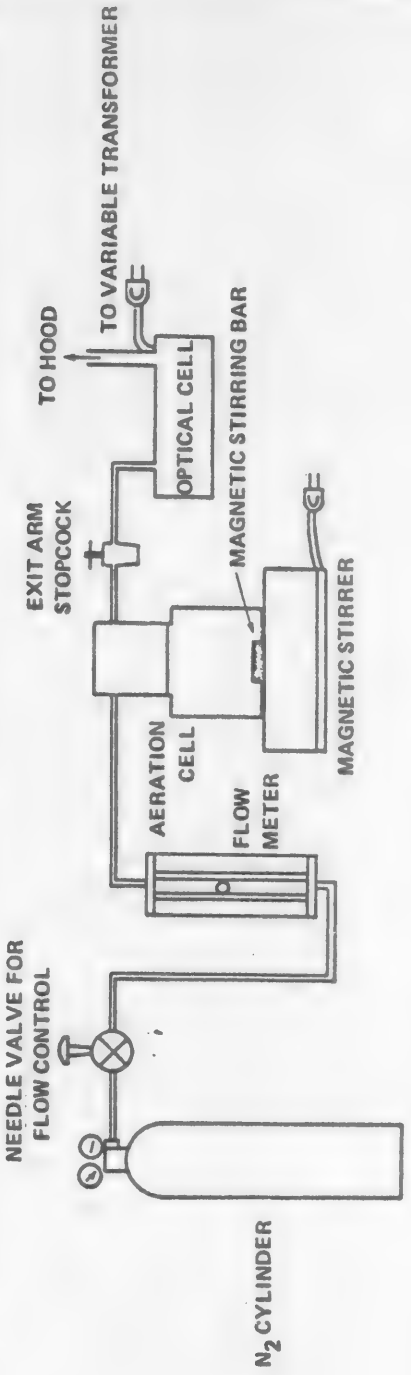

Figure 101-5. Schematic of aeration system.

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8.2 Optical Cell Heating System Calibration. Using a 50-ml graduated cylinder, add 50-ml of deionized distilled water to the bottle section of the aeration cell and attach the bottle section to the bubbler section of the cell. Attach the aeration cell to the optical cell; and while aerating at 1.5 liters/min, determine the minimum variable transformer setting necessary to prevent condensation of moisture in the optical cell and in the connecting tubing. (This setting should not exceed 20 volts.)

8.3 Spectrophotometer and Recorder Calibration. (Note: The temperature of the solution affects the rate at which elemental Hg is released from a solution and, consequently, it affects the shape of the absorption curve (area) and the point of maximum absorbance (peak height). Therefore, to obtain reproducible results, bring all solutions to room temperature before use.) Set the spectrophotometer wavelength at 253.7 nm, and make certain the optical cell is at the minimum temperature that will prevent water condensation. Then set the recorder scale as follows: Using a 50-ml graduated cylinder, add 50-ml of deionized distilled water to the aeration cell bottle and pipet 5.0 ml of the working mercury standard solution into the aeration cell.

Note.—Always add the Hg-containing solution to the aeration cell *after* the 50-ml of deionized distilled water.

Place a Teflon-coated stirring bar in the bottle. Before attaching the bottle section to the bubbler section of the aeration cell, make certain that (1) the aeration cell exit arm stopcock (Figure 101–3) is closed (so that Hg will not prematurely enter the optical cell when the reducing agent is being added) and (2) there is no flow through the bubbler. If conditions (1) and (2) are met, attach the bottle section to the bubbler section of the aeration cell. Pipet 5 ml. of stannous chloride solution into the aeration cell through the sidearm of the cell and immediately stopper the sidearm. Stir the solution for 15 sec, turn on the recorder, open the aeration cell exit arm stopcock, and then immediately initiate aeration with continued stirring. Determine the maximum absorbance of the standard and set this value to read 90 percent of the recorder full scale.

8.4 Calibration Curve. After setting the recorder scale, repeat the procedure in section 8.3 using 0.0-, 1.0-, 2.0-, 3.0-, 4.0-, and 5.0-ml aliquots of the working standard solution (final amount of Hg in the aeration cell is 0, 200, 400, 600, 800, and 1000 ng, respectively). Repeat this procedure on each aliquot size until two consecutive peaks agree within 3 percent of their average value. (Note: To prevent Hg carry-over from one sample to another, do not close the nitrogen tank valve and do not disconnect the aeration cell from the optical cell until the recorder pen has returned to the base line.) It should not be necessary to disconnect the aeration gas inlet line from the aeration cell when changing samples. After separating the bottle and bubbler sections of the aeration cell, place the bubbler section into a 600-ml beaker containing approximately 400-ml of deionized distilled water. Rinse the bottle section of the aeration cell with a stream of deionized distilled water to remove all traces of the tin(II) reducing agent. Also, to prevent the loss of Hg before aeration, remove all traces of the reducing agent between samples by washing with deionized distilled water. It will be necessary, however, to wash the aeration cell parts with concentrated HC1 if any of the following conditions occur: (1) a white film appears on any inside surface of the aeration cell, (2) the calibration curve changes suddenly, or (3) the replicate samples do not yield reproducible results.

Subtract the average peak height of the blank (0.0-ml aliquot)—which should be less than 2 percent of recorder full scale—from the averaged peak heights of the 1.0-, 2.0-, 3.0-, 4.0-, and 5.0-ml aliquot standards. If the blank absorbance is greater than 2 percent of full-scale, the probable cause is Hg contamination of a reagent or carry-over of Hg from a previous sample. Plot the corrected peak height of each standard solution versus the corresponding final total Hg weight in the aeration cell (in ng) and draw the best-fit straight line. This line should either pass through the origin or pass through a point no further from the origin than ± 2 percent of the recorder full-scale. If the line does not pass through or very near to the origin, check for nonlinearity of the curve and for incorrectly prepared standards.

8.5 Sampling Train Calibration. Calibrate the sampling train components according to the procedures outlined in the following sections of Method 5: Section 5.1 (Probe Nozzle), section 5.2 (Pitot Tube), section 5.3 (Metering System), section 5.4 (Probe Heater), section 5.5 (Temperature Gauges), section 5.7 (Barometer). Note that the leak-check described in section 5.6 of Method 5 applies to this method.

9. *Calculations.*

9.1 Dry Gas Volume. Using the data from this test, calculate $V_{m(std)}$, the dry gas sample volume at standard conditions (corrected for leakage, if necessary) as outlined in Section 6.3 of Method 5.

9.2 Volume of Water Vapor and Moisture Content. Using the data obtained from this test, calculate the volume of water vapor $V_{w(std)}$ and the moisture content B_{ws} of the stack gas. Use Equations 5–2 and 5–3 of Method 5.

9.3 Stack Gas Velocity. Using the data from this test and Equation 2–9 of Method 2, calculate the average stack gas velocity v_s.

9.4 Total Mercury. For each source sample, correct the average maximum absorbance of the two consecutive samples whose peak heights agree within ± 3 percent of their average for the contribution of the solution blank (see 8.4). Use the calibration curve and these corrected averages, to determine the final Hg concentration $C_{Hg(AC)}$ in the aeration cell for each source sample. Correct for any dilutions made to bring the sample in the working range of the spectrophotometer. Then calculate the Hg in μg (M_{Hg}) in the original solution as follows:

$$m_{Hg} = \frac{C_{Hg(AC)}\ (D.F.)\ V_f\ 10^{-3}}{S} \qquad \text{Eq. 101-1}$$

Where:

D.F. = Dilution factor for the Hg-containing solution (before adding to the aeration cell; e.g.,

D.F. = 250/2 if the source samples were diluted as described in section 7.3.3.

V_f = Solution volume of original sample, 1000 ml for samples diluted as described in 7.2.1.

10^{-3} = Conversion factor, μg/ng.

S = Aliquot volume added to aeration cell, ml.

9.5 Mercury Emission Rate. Calculate the Hg emission rate R in g/day for continuous operations using Equation 101–2. For cyclic operations, use only the time per day each stack is in operation. The total Hg emission rate from a source will be the summation of results from all stacks.

$$R = K\ \frac{m_{Hg}\ v_s\ A_s\ (86{,}400 \times 10^{-6})}{[V_{m(std)} + V_{w(std)}](T_s/P_s)} \qquad \text{Eq. 101-2}$$

Where:

A_s = Stack cross-sectional area, m^2 (ft^2).

86,400 = Conversion factor, sec/day.

10^{-6} = Conversion factor, μg/g.

T_s = Absolute average stack gas temperature, °K (°R).

P_s = Absolute stack gas pressure, mm Hg (in. Hg).

K = 0.3858 °k/mm Hg for metric units.
= 17.64 °R in. Hg for English units.

9.6 Isokinetic Variation and Acceptable Results. Same as Method 5, sections 6.11 and 6.12, respectively.

9.7 Determination of Compliance. Each performance test consists of three repetitions of the applicable test method. For the purpose of determining compliance with an applicable national emission standard, use the average of the results of all repetitions.

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Method 102. Determination of Particulate and Gaseous Mercury Emissions From Chlor-Alkali Plants—Hydrogen Streams

1. *Introduction.*

Although similar to Method 101, Method 102 requires changes to accommodate the sample being extracted from a hydrogen stream. Conduct the test according to Method 101, except as shown below:

2. *Mercury Train Operation.*

2.1 Probe Heating System. Do not use, unless otherwise specified.

2.2 Glass Fiber Filter. Do not use, unless otherwise specified.

2.3 Safety Procedures. The sampler must conduct the source test under conditions of utmost safety, because hydrogen and air mixtures are explosive. Since the sampling train essentially is leakless, attention to safe operation can be concentrated at the inlet and outlet. If a leak does occur, however, remove the meter box cover to avoid a possible explosive. The following specific precautions are recommended:

2.3.1 Operate only the vacuum pump during the test. The other electrical equipment, e.g., heaters, fans, and timers, normally are not essential to the success of a hydrogen stream test.

2.3.2 Seal the sample port to minimize leakage of hydrogen from the stack.

2.3.3 Vent sampled hydrogen at least 3 m (10 ft) away from the train. This can be accomplished by attaching a 13-mm-ID (0.50-in.) Tygon [3] tube to the exhaust from the orifice meter.

Note.—A smaller ID tubing may cause the orifice meter calibration to be erroneous. Take care to ensure that the exhaust line is not bent or pinched.

2.4 Setting of Isokinetic Rates.

2.4.1 If a nomograph is used, take special care in the calculation of the molecular weight of the stack gas and in the setting of the nomograph to maintain isokinetic conditions during sampling (sections 2.4.1.1 through 2.4.1.3 below).

2.4.1.1 Calibrate the meter box orifice. Use the techniques described in APTD-0576 (see Citation 9 in section 10 of Method 101). Calibration of the orifice meter at flow conditions that simulate the conditions at the source is suggested. Calibration should either be done with hydrogen or with some other gas having a similar Reynolds Number so that there is similarity between the Reynolds Numbers during calibration and during sampling.

2.4.1.2 The nomograph described in APTD-0576 cannot be used to calculate the C factor because the nomograph is designed for use when the stack gas dry molecular weight is 29 ± 4. Instead, the following calculation should be made to determine the proper C factor:

$$C = 0.00154\ \Delta H@\ C_p^{\,2}\ T_m\ (P_s/P_m)\ \frac{(1 - B_{ws})^2}{(1 - B_{ws}) + 1.8\ B_{ws}/M_d}$$

Where:

$\Delta H@$ = Meter box calibration factor obtained in section 2.4.1.1, in. H_2O.

C_p = Pitot tube calibration coefficient, dimensionless.

T_m = Absolute temperature of gas at the orifice, °R.

P_s = Absolute pressure of stack gas, in. Hg.

P_m = Absolute pressure of gas at the meter, in. Hg.

B_{ws} = Fraction by volume of water vapor in the stack gas.

M_d = Dry molecular weight of stack gas, lb/lb-mole.

Note.—This calculation is left in English units, and is not converted to metric units because nomographs are based on English units.

2.4.1.3 Set the calculated C factor on the operating nomograph and select the proper nozzle diameter and K factor as specified in APTD–0576. If the C factor obtained in section 2.4.1.2 exceeds the values specified on the existing operating nomograph, expand the C

[3] Mention of trade names or specific products does not constitute endorsement by the U.S. Environmental Protection Agency.

scale logarithmically so that the values can be properly located.

2.4.2 If a calculator is used to set isokinetic rates, it is suggested that the isokinetic equation presented in Citation 17 in the Bibliography of Method 101 be used.

2.5 Sampling is Small (< 12-in.-Diameter) Stacks. When the stack diameter (or equivalent diameter) is less than 12 inches, conventional pitot-tube probe assemblies should not be used. For sampling guidelines, see Citation 18 in the Bibliography of Method 101.

2. By adding Method 111 to Appendix B—Test Methods as follows:

Appendix B—Test Methods

* * * * *

Method 111. Determination of Particulate and Gaseous Mercury Emissions From Sewage Sludge Incinerators

Introduction

This method is similar to Method 101, except acidic potassium permanganate solution is used instead of acidic iodine monochloride for collection.

1. *Applicability and Principle.*

1.1 Applicability. This method applies to the determination of particulate and gaseous mercury (Hg) emissions from sewage sludge incinerators and other sources as specified in the regulations.

1.2 Principle. Particulate and gaseous Hg emissions are withdrawn isokinetically from the source and collected in acidic potasium permanganate ($KMnO_4$) solution. The Hg collected (in the mercuric form) is reduced to elimental Hg, which is then aerated from the solution into an optical cell and measured by atomic absorption spectrophotometry.

2. *Range and Sensitivity.*

2.1 Range. After initial dilution, the range of this method is 20 to 800 ng Hg/ml. The upper limit can be extended by further dilution of the sample.

2.2 Sensitivity. The sensitivity of the method depends on the recorder/spectrophotometer combination selected.

3. *Interfering Agents.*

3.1 Sampling. Excessive oxidizable organic matter in the stack gas prematurely depletes the $KMnO_4$ solution and thereby prevents further collection of Hg.

3.2 Analysis. Condensation of water vapor on the optical cell windows causes a positive interference.

4. *Precision.*

Based on eight paired-train tests, the within-lalboratory standard deviation was estimated to be 4.8 μg Hg/ml in the concentration range of 50 to 130 μg Hg/m^3.

5. *Apparatus.*

5.1 Sampling Train and Sample Recovery. Same as Method 101, sections 5.1 and 5.2, respectively, except for the following variations:

5.1.1 Probe Liner. Same as Method 101, section 5.1.2, except that if a filter is used ahead of the impingers, the tester must use the probe heating system to minimize the condensation of gaseous Hg.

5.1.2 Filter Holder (Optional). Borosilicate glass with a rigid stainless-steel wire-screen filter support (do not use glass frit supports) and a silicone rubber or Teflon gasket, designed to provide a positive seal against leakage from outside or around the filter. The filter holder must be equipped with a filter heating system capable of maintaining a temperature atound the filter holder of 120 ± 15°C (248 ± 25°F) during sampling to minimize both water and gaseous Hg condensation. The tester may use a filter in cases where the stream contains large quantities of particulate matter.

5.2 Analysis. The apparatus needed for analysis is the same as Method 101, section 5.3, except as follows:

5.2.1 Volumetric Pipets. Class A; 1-, 2-, 3-, 4-, 5-, 10-, and 20-ml.

5.2.2. Graduated cylinder. 25-ml.

5.2.3. Steam Bath.

6. *Reagents.*

Use ACS reagent-grade chemicals or equivalent, unless otherwise specified.

6.1 Sampling and Recovery. The reagents used in sampling and recovery are as follows:

6.1.1 Water. Deionized, distilled, meeting ASTM Specifications for Type I Reagent Water—ASTM Test Method D 1193–72. If high concentrations of organic matter are not expected to be present, the analyst may eliminate the $KMnO_4$ test for oxidizable organic matter. Use this water in all dilutions and solution preparations.

6.1.2 Nitric Acid (HNO_3), 50 Percent (V/V). Mix equal volumes of concentrated HNO_3 and dseionized distilled water.

6.1.3 Silica Gel. Indicating type, 6- to 16-mesh. If previously used, dry at 175°C (350°F) for 2 hr. The tester may use new silica gel as received.

6.1.4 Filter (Optional). Glass fiber filter, without organic binder, exhibiting at least 99.95 percent efficiency on 0.1 μm dioctyl phthalate smoke particles. The tester may use the filter in cases where the gas stream contains large quantities of particulate matter, but he should analyze blank filters for Hg content.

6.1.5 Sulfuric Acid (H_2SO_4), 10 Percent (V/V). Mix 100 ml of concentrated H_2SO_4 with 900 ml of deionized distilled water.

6.1.6 Absorbing Solution, 4 Percent $KMnO_4$ (W/V). Prepare fresh daily. Dissolve 40 g of $KMnO_4$ in sufficient 10 percent H_2SO_4 to make 1 liter. Prepare and store in glass bottles to prevent degradation.

6.2 Analysis. The reagents needed for analysis are listed below:

6.2.1 Tin(II) Solution. Prepare fresh daily and keep sealed when not being used. Completely dissolve 20 g of tin(II) chloride (or 25 g of tin(II) sulfate) crystals (Baker Analyzed [4] reagent grade or any other brand that will give a clear solution) in 25 ml of concentrated HCl. Dilute to 250 ml with deionized distilled water. Do not substitute HNO_3, H_2SO_4, or other strong acids for the HCl.

6.2.2 Sodium Chloride—Hydroxylamine Solution. Dissolve 12 g of soldium chloride and 12 g of hydroxylamine sulfate (or 12 g of hydroxylamine hydrochloride) in deionized distilled water and dilute to 100 ml.

6.2.3 Hydrochloric Acid (HCl), 8 N. Dilute 67 ml of concentrated HCl to 100 ml with deionized distilled water.

6.2.4 Nitric Acid, 15 Percent (V/V). Dilute 15 ml of concentrated HNO_3 to 100 ml with deionized distilled water.

6.2.5 Mercury Stock Stock Solution, 1 mg HG/ml. Completely dissolve 0.1354 g of mercury(ii) chloride in 75 ml of deionized distilled water. Add 10 ml of concentrated HNO_3, and adjust the volume to exactly 100 ml with deionized distilled water. Mix thoroughly. This solution is stable for at least 1 month.

6.2.6 Intermediate Mercury and Standard Solution, 10 μg Hg/ml. Prepare fresh weekly. Pipet 5.0 ml of the mercury stock solution (6.2.5) into a 500-ml volumetric flask and add 20 ml of 15 percent HNO_3 solution. Adjust the volume to exactly 500 ml with deionized distilled water. Thoroughly mix the solution.

6.2.7 Working Mercury Standard Solution, 200 ng Hg/ml. Prepare fresh daily. Pipet 5.0 ml from the "Intermediate Mercury Standard Solution" (6.2.6) into a 250-ml volumetric flask. Add 5 ml of 4 percent $KMnO_4$ absorbing solution and 5 ml of 15 percent HNO_3. Adjust the volume to exactly 250 ml with deionized distilled water. Mix thoroughly.

6.2.8 Potassium Permanganate, 5 Percent (W/V). Dissolve 5 g of $KMnO_4$

[4] Mention of trade names or specific products does not constitute endorsement by the U.S. Environmental Protection Agency.

in deionized distilled water and dilute to 100 ml.

6.2.9 Filter. Whatman No. 40 or equivalent.

7. *Procedure.*

7.1 Sampling. The sampling procedure is the same as Method 101, except for changes due to the use of $KMnO_4$ instead of ICl absorbing solution and the possible use of a filter. These changes are as follows:

7.1.1 Preliminary Determinations. The preliminary determinations are the same as that given in Method 101, section 7.1.2, except for the absorbing solution depletion sign. In this method, high oxidizable organic content may make it impossible to sample for the desired minimum time. This problem is indicated by the complete bleaching of the purple color of the $KMnO_4$ solution. In these cases, the tester may divide the sample run into two or more subruns to insure that the absorbing solution would not be depleted.

7.1.2 Preparation of Sampling Train. The preparation of the sampling train is the same as that given in Method 101, section 7.1.3, except for the cleaning of the glassware [probe, filter holder (if use), impingers, and connectors] and the charging of the first three impingers. In this method, clean all the glass components by rinsing with 50 percent HNO_3, tap water, 8 N HCl, tap water, and finally deionized distilled water. Then place 50 ml of 4 percent $KMnO_4$ in the first impinger and 100 ml in each of the second and third impingers.

If a filter is used, use a pair of tweezers to place the filter in the filter holder. Be sure to center the filter and place the gasket in proper position to prevent the sample gas stream from bypassing the filter. Check the filter for tears after assembly is completed. Be sure also to set the filter heating system at the desired operating temperature after the sampling train has been assembled.

7.1.3 Sampling Train Operation. In addition to the procedure given in Method 101, section 7.1.5, maintain a temperature around the filter (if applicable) of 120°±14°C (248°±25°F).

7.2 Sample Recovery. Begin proper cleanup procedure as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool. When it can be safely handled, wipe off any external particulate matter near the tip of the probe nozzle and place a cap over it. Do not cap off the probe tip tightly while the sampling train is cooling because the resultant vacuum would draw liquid out from the impingers.

Before moving the sample train to the cleanup site, remove the probe from the train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the impinger. Use either ground-glass stoppers, plastic caps, or serum caps to close these openings.

Transfer the probe, impinger assembly, and (if applicable) filter assembly to a cleanup area that is clean, protected from the wind, and free of Hg contamination. The ambient air in laboratories located in the immediate vicinity of Hg-using facilities is not normally free of Hg contamination.

Inspect the train before and during assembly, and note any abnormal conditions. Treat the sample as follows:

7.2.1 *Container No. 1* (Impinger, Probe, and Filter Holder). Use a graduated cylinder; measure the liquid in the first three impingers to within ± 1 ml. Record the volume of liquid present (e.g., see Figure 5–3 of Method 5). This information is needed to calculate the moisture content of the effluent gas. (Use only graduated cylinder and glass storage bottles that have been precleaned as in section 7.1.2.) Place the contents of the first three impingers into a 1000-ml glass sample bottle.

Note.—If a filter is used, remove the filter from its holder, as outlined under "Container No. 3" below.

Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover the Hg (and any condensate) from the probe nozzle, probe fitting, probe liner and front half of the filter holder (if applicable) as follows: Rinse these components with a total of 250 to 400 ml of fresh 4 percent $KMnO_4$ solution. Add all washings to the 1000-ml glass sample bottle. Remove any residual brown deposits on the glassware using the minimum amount of 8 N HC1 required and add this HC1 rinse to this sample container.

After all washings have been collected in the sample container, tighten the lid on the container to prevent leakage during shipment to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to clearly identify its contents.

7.2.2 *Container No. 2* (Silica Gel). Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. Transfer the silica gel from its impinger to its original container, and seal. The tester may use as aids a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. It is not necessary to remove the small amount of particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g; record this weight.

7.2.3 *Container No. 3* (Filter). If a filter was used, carefully remove it from the filter holder, place it in a 100-ml glass sample bottle, and add 20 to 40 ml of 4 percent $KMnO_4$. If it is necessary to fold the filter, be sure that the particulate cake is inside the fold. Carefully transfer to the 150-ml sample bottle any particulate matter and/or filter fibers that adhere to the filter holder gasket by using a dry Nylon bristle brush and/or a sharp-edge blade. Seal the container. Label the container to clearly identify its contents. Mark the height of the fluid level to determine whether leakage occurs during transport.

7.2.4 *Container No. 4* (Filter Blank). If a filter was used, treat an unused filter from the same filter lot used for sampling in the same manner as Container No. 3.

7.2.5 *Container No. 5* (Absorbing Solution Blank). For a blank, place 500 ml of 4 percent $KMnO_4$ absorbing solution in a 1000-ml sample bottle. Seal the container.

7.3 Sample Preparation. Check liquid level in each container to see if liquid was lost during transport. If a noticeable amount of leakage occurred, either void the sample or use methods subject to the approval of the Administrator to account for the losses. Then follow the procedures below.

7.3.1 *Containers No. 3 and No. 4* (Filter and Filter Blank). If a filter was used, place the contents, including the filter, of Containers No. 3 and No. 4 in separate 250-ml beakers and heat the beakers on a steam bath until most of the liquid has evaporated. Do not take to dryness. Add 20 ml of concentrated HNO_3 to the beakers, cover them with a glass, and heat on a hot plate at 70°C for 2 hrs. Remove from the hot plate and filter the solution through Whatman No. 40 filter paper. Save the filtrate for Hg analysis. Discard the filter.

7.3.2 *Container No. 1* (Impingers, Probe, and Filter Holder). Filter the contents of Container No. 1 through Whatman 40 filter paper to remove the brown MnO_2 precipitate. Wash the filter with 50 ml of 4 percent $KMnO_4$ absorbing solution and add this wash to the filtrate. Discard the filter. Combine the filtrates from Containers No. 1 and No. 3 (if applicable), and dilute to a

known volume with deionized distilled water. Mix thoroughly.

7.3.3 *Container No. 5* (Absorbing Solution Blank). Treat this container as described in section 7.3.2. Combine this filtrate with the filtrate from Container No. 4 and dilute to a known volume with deionized distilled water. Mix thoroughly.

7.4 Analysis. Calibrate the spectrophotometer and recorder and prepare the calibration curve as described in sections 8.1 to 8.4. Then repeat the procedure used to establish the calibration curve with appropriately sized aliquots (1 to 10 ml) of the samples (from sections 7.3.2 and 7.3.3) until two consecutive peak heights agree within ±3 percent of their average value. If the 10-ml sample is below the detectable limit, use a larger aliquot (up to 20 ml), but decrease the volume of water added to the aeration cell accordingly to prevent the solution volume from exceeding the capacity of the aeration bottle. If the peak maximum of a 1.0-ml aliquot is off scale, further dilute the original sample to bring the Hg concentration into the calibration range of the spectrophotometer. If the Hg content of the absorbing solution and filter blank is below the working range of the analytical method, use zero for the blank.

Run a blank and standard at least after every five samples to check the spectrophotometer calibration; recalibrate as necessary.

It is also recommended that at least one sample from each stack test be checked by the Method of Standard Additions to confirm that matrix effects have not interfered in the analysis.

8. *Calibration and Standards.*

Before use, clean all glassware, both new and used, as follows: Brush with soap and water, liberally rinse with tap water, soak for 1 hour in 50 percent of HNO_3, and then rinse with deionized distilled water.

8.1 Flow Calibration. Assemble the aeration system as shown in Figure 101–5 of Method 101. Set the outlet pressure on the nitrogen cylinder regulator to a minimum pressure of 500 mm Hg (10 psi), and use the flow metering valve and a bubble flow meter or wet test meter to obtain a flow rate of 1.5 ± 0.1 liters/min through the aeration cell. After the flow calibration is complete, remove the bubble flow meter from the system.

8.2 Optical Cell Heating System Calibration. Using a 25-ml graduated cylinder, add 25 ml of deionized distilled water to the bottle section of the aeration cell and attach the bottle section to the bubbler section of the cell. Attach the aeration cell to the optical cell; and while aerating at 1.5 liters/min, determine the minimum variable transformer setting necessary to prevent condensation of moisture in the optical cell and in the connecting tubing. (This setting should not exceed 20 volts.)

8.3 Spectrophotometer and Recorder Calibration.

Note.—The temperature of the solution affects the rate at which elemental Hg is released from a solution and, consequently, it affects the shape of the absorption curve (area) and the point of maximum absorbance (peak height). To obtain reproducible results, all solutions must be brought to room temperature before use.

Set the spectrophotometer wavelength at 253.7 nm and make certain the optical cell is at the minimum temperature that will prevent water condensation. Then set the recorder scale as follows: Using a 25-ml graduated cylinder, add 25 ml of deionized distilled water to the aeration cell bottle and pipet 5.0 ml of the working mercury standard solution into the aeration cell.

Note.—Always add the Hq-containing solution to the aeration cell *after* the 25 ml of deionized distilled water.

Place a Teflon-coated stirring bar in the bottle. Add 5 ml of the 4 percent $KMnO_4$ absorbing solution followed by 5 ml of 15 percent HNO_3 and 5 ml of 5 percent $KMnO_4$ to the aeration bottle and mix well. Now, attach the bottle section to the bubbler section of the aeration cell and make certain that (1) the aeration cell exit arm stopcock (Figure 101–3 of Method 101) is closed (so that Hg will not prematurely enter the optical cell when the reducing agent is being added) and (2) there is no flow through the bubbler. Add 5 ml of sodium chloride hydroxylamine in 1-ml increments until the solution is colorless. Now add 5 ml of tin(II) solution to the aeration bottle through the side-arm and immediately stopper the side-arm. Stir the solution for 15 sec, turn on the recorder, open the aeration cell exit arm stopcock, and immediately initiate aeration with continued stirring. Determine the maximum absorbance of the standard and set this value to read 90 percent of the recorder full scale.

8.4 Calibration Curve. After setting the recorder scale, repeat the procedure in section 8.3 using 0.0-, 1.0-, 2.0-, 3.0-, 4.0-, and 5.0-ml aliquots of the working standard solution (final amount of Hg in the aeration cell is 0, 200, 400, 600, 800, and 1000 ng, respectively). Repeat this procedure on each aliquot size until two consecutive peaks agree within 3 pecent of their average value.

Note.—To prevent Hg carryover from one sample to another, do not close the nitrogen tank valve and do not disconnect the aeration cell from the optical cell until the recorder pen has returned to the base line. It should not be necessary to disconnect the aeration gas inlet line from the aeration cell when changing samples. After separating the bottle and bubbler sections of the aeration cell, place the bubbler section into a 600-ml beaker containing approximately 400 ml of deionized distilled water and rinse the bottle section of the aeration cell with a stream of deionized distilled water to remove all traces of the tin(II) reducing agent. Also, to prevent the loss of Hg before aeration, remove all traces of the reducing agent between samples by washing with deionized distilled water. It will be necessary, however, to wash the aeration cell parts with concentrated HCl if any of the following conditions occur: (1) a white film appears on any inside surface of the solution cell, (2) the calibration curve changes suddenly, or (3) the replicate samples do not yield reproducible results.

Subtract the average peak height of the solution blank (0.0-ml aliquot)—which should be less than 2 percent of recorder full scale—from the averaged peak heights of the 1.0-ml, 2.0-ml, 3.0-ml, 4.0-ml, and 5.0-ml aliquot standards. If the blank absorbance is greater than 2 percent of full-scale, the probable cause is Hg contamination of a reagent or carry-over of Hg from a previous sample. Plot the corrected peak height of each standard solution versus the corresponding final total Hg weight in the aeration cell (in ng) and draw the best fit straight line. This line should either pass through the origin or pass through a point no further from the origin than ±2 percent of the recorder full scale. If the line does not pass through or very near to the origin, check for nonlinearity of the curve and for incorrectly prepared standards.

8.5 Sampling Train Calibraton. Calibrate the sampling train components according to the procedures outlined in the following sections of Method 5: section 5.1 (Probe Nozzle); section 5.2 (Pitot Tube); section 5.3 (Metering Sytem); section 5.4 (Probe Heater); section 5.5 (Temperature Gauges); section 5.7 (Barometer). Note that the leak check described in section 5.6 of Method 5 applies to this method.

9. *Calculations.*

9.1 Dry Gas Volume, Volume of Water Vapor and Moisture Content, Stack Gas Velocity, Isokinetic Variation and Acceptable Results, and Determination of Compliance. Same as Method 101, sections 9.1, 9.2, 9.3, 9.6, and 9.7, respectively, except use data obtained from this test.

9.2 Total Mercury. For each source sample, correct the average maximum absorbance of the two consecutive samples whose peak heights agreed within ± 3 percent of their average for the contribution of the field blank. Then

calculate the total Hg content in μg in each sample. Correct for any dilutions made to bring the sample into the working range of the spectrophotometer.

9.3 Mercury Emission Rate. Calculate the Hg emission rate R in g/day for continuous operations using Equation 111–1. For cyclic operations, use only the time per day each stack is in operation. The total Hg emission rate from a source will be the summation of results from all stacks.

$$R = \frac{K\, m_{Hg}\, v_s\, A_s\, (86{,}400 \times 10^{-6})}{[V_{m(std)} + V_{w(std)}]\,(T_s/P_s)} \qquad \text{Eq. 111-1}$$

Where:

m_{Hg} = Total Hg content in each sample, μg.

v_s = Average stack gas velocity, m/sec (fps).

A_s = Stack cross-sectional area, m^2 (ft^2).

86,400 = Conversion factor, sec/day.

10^{-6} = Conversion factor, μg.

$V_{m(std)}$ = Dry gas sample volume at standard conditions, corrected for leakage (if any), m^3 (ft^3).

$V_{w(std)}$ = Volume of water vapor at standard conditions, m^3 (ft^3).

T_s = Absolute average stack gas temperature, °K (°R).

P_s = Absolute stack gas pressure, mm Hg (in. Hg).

K = 0.3858 °K/mm Hg for metric units.
= 17.64 °R/in. Hg for English units.

10. *Bibliography.*

1. Same as Method 101, section 10.

2. Mitchell, W. J., M. R. Midgett, J. C. Suggs, and D. Albrinck. Test Methods to Determine the Mercury Emissions from Sludge Incineration Plants. U.S. Environmental Protection Agency. Research Triangle Park, North Carolina. Publication No. EPA–600/4–79–058. September 1979.

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